BEYOND VPTn-SCTST FOR CHEMICAL KINETICS: COMPLEX SCALING AND CURVILINEAR VIBRATIONAL SELF-CONSISTENT FIELD THEORY

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Semi-classical transition state theory (SCTST) is a powerful tool for calculating quantitative chemical reaction rates based on local properties of the transition state (TS) itself without detailed knowledge of the entire reaction path. The widely successful variant of SCTST based on second-order vibrational perturbation theory (VPT2) routinely provides accurate kinetic rate predictions. However, the fundamental formulation and approximations of VPT2 (and higher order extensions) often cause it to fail in the presence of significant anharmonicity near the TS. Curvilinear vibrational self consistent field theory (VSCF) together with its second order perturbative extension (VMP2) are an effective alternative to standard VPT2 for the bound state vibrational problem of highly anharmonic PES minima, suggesting similar improvements are possible at the TS. This talk will present some ideas and exploratory results towards applying complex scaled VSCF to the TS problem.